

ASSOCIATION BEHAVIORS OF COAL-DERIVED MATERIALS IN ORGANIC SOLVENTS

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INTRODUCTION

Coal-derived materials such as coal extracts and liquefaction products are known to readily associate in organic solvents(1,2). Hydrogen bonds and aromatic π - π interactions are considered to be main associative interactions, though charge transfer and ionic interactions possibly contribute to the associations. Many studies on this topic have been carried out so far, since these association behaviors strongly affect solubility, boiling point, viscosity, and other physical properties at their bulk or solution state, which are key properties in the operation of coal conversion processes.

This topic is also related to controversial issue in coal structure i.e., covalent crosslinking network or non-covalent (molecular associated) network. Coal swells in an organic solvent and a swollen coal shows elastic behaviors. So, it is sure that coal has a kind of network structure. Although covalently connected crosslinking network structures are often assumed so far, there is no clear evidence for them. Recent works (3-5) suggest that at least for some bituminous coals, non-covalently connected network, i.e., associate structures of coal molecules are a better model than the covalent ones.

Here, association behaviors of coal-derived materials will be reviewed and discussed from solubility, molecular weight, viscosity, surface tension, small angle neutron scattering, and computer simulation, compared with petroleum asphaltenes in solution. Thermodynamics of the solution will also be discussed from sol-gel transition phenomena.

RESULTS AND DISCUSSION

Solubilities.

It is well known that the solubilities of coal-derived materials increase by silylation, i.e., $\text{OH} \rightarrow \text{OSi}(\text{CH}_3)_3$ or acylation of OH groups. This can be attributed to loss of intermolecular hydrogen bonds among coal molecules. Similarly, the pyridine extraction yields of a high-rank bituminous coal (89.6 carbon %) increases from 5% to 90 % by C-octylation at carbons such as benzylic methylene carbons, probably due to the disruption of the π - π stacking of aromatic rings by the introduction of the large octyl group. (6)

We found (7, 8) that a 1:1 carbon disulfide / *N*-methyl-2-pyrrolidinone (CS_2 / NMP) mixed solvent gave high extraction yields, more than 50 wt%, for several bituminous coals at room temperature. No significant bond cleavage has been observed to occur during the extraction. The extracts obtained, i.e., the mixed solvent soluble fractions, were further fractionated with acetone and pyridine into acetone soluble (AS) fraction, acetone insoluble / pyridine soluble (PS) fraction, and pyridine insoluble (PI) fraction which is a heavier fraction than preasphaltenes. We also have found that 30 - 50 % of PI became insoluble in the extraction mixed solvent, but the solubilities recovered by the re-addition of the separated extract fractions (AS and PS) or the addition of the compounds which have strong interaction with coal molecules, to PI (9, 10). Especially, tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ) were found to be very effective. The studies on IR spectra of the extract fractions and reversibility of the effect of TCNE addition suggest that the solubility increase is caused by the breaking of noncovalent bonds in associated structures of coal molecules by TCNE, which interact and form new associates with coal molecules which are soluble in the mixed solvent.

Molecular Weight

Hombach(11,12) indicated that usual osmometric methods including VPO is not recommended for molecular weight determinations for complex coal-derived substances, since the van't Hoff equation used for osmotic pressure is not applicable for the substances with polydispersed molecular weights and inhomogeneous chemical structures such as coal asphaltenes. Collins et al.(13) also suggested that there is no accurate method for the molecular weight determinations of coal-derived substances, since coal solutions can not be viewed as a solution of a series of polymer homologues which is a necessary condition for use of osmotic or light-scattering methods. Hombach(12) has reported that a fraction obtained by ultrafiltration (0.2 and 0.035 μm pore filter) in pyridine solution of pyridine extract from a solubilized bituminous coal have very high molecular weights, i.e., 1.59×10^6 using a low-angle laser light-scattering method. Larsen et al.(14) showed that for relatively low molecular weight coal-derived substances mass spectrometry is available, and molecular weights determined by ^{252}Cf plasma desorption mass spectrometry are in good agreement with those obtained by field ionization mass spectrometry and gel permeation chromatography. Asphaltenes from distillation residues of liquefaction products of various coals have 260 - 330 of number-average molecular weight by ^{252}Cf plasma

desorption mass spectrometry.

Lee et al.(15) used VPO as a means for determination of degree of association of coal-derived substances. From the relation between molecular weight and concentration of coal-derived substances in solution, the dissociation constants of dimer, trimer, and higher multimers, and their distribution change with concentration were determined.

Viscosity

Viscosity of coal-derived substances in solution and bulk is related to their associated structures, and in coal liquefaction processes it is important to control high viscosity of coal - solvent mixtures. Bockrath et al.(16) measured the viscosities of preasphaltene, asphaltene (and its acid / neutral and basic components), and oil (pentane soluble) of coal-derived liquids from liquefaction. The viscosity of the mixtures of various compositions of acid / neutral and basic asphaltenes for fixed total asphaltene fraction (30 % asphaltene in oil) was found to be greater than would be expected on the basis of a simple additive relationship, suggesting that hydrogen bonding between acid / neutral with basic asphaltenes increases viscosity. The preasphaltenes, on a weight basis, have approximately twice the effect on viscosity as do the asphaltenes, probably due to their larger molecular weight and functionality in comparison to the asphaltenes. Bockrath et al.(17) also have showed that intermolecular association involving hydrogen bonding is a prime factor for the viscosity increase which occurred with increased asphaltene concentration in a reference solvent. Similarly the importance of hydrogen bonds largely involving phenolic OH in the viscosity increase was suggested.(18) Arganinski and Jones(19,20) also suggest that the influence on the viscosity of coal-derived preasphaltenes and model compounds in THF was the order hydrogen bonding > molecular weight >> degree of aromatic condensation (charge transfer interaction).

Surface Tension

Surface tension is used for analyzing colloidal properties such as micelles formation. We(21) measured the surface tension of *N*-methyl-2-pyrrolidinone (NMP) solution of acetone soluble (AS) and acetone insoluble / pyridine soluble (PS) fractions of the CS₂/ NMP mixed solvent extract of a bituminous coal by the Wilhelmy method. The surface tensions of the solutions freshly prepared by the dilution of the concentrated solution with NMP changed with time, and it took several hours to attain an equilibrium state of lower surface tension. This suggests that the rate of the re-construction to a new association state are very slow. The equilibrium surface tensions of NMP solution of AS decreases with AS concentration and a discontinuity point at some concentration (0.1 - 0.3 g/dL for two different AS's) are observed, where the slope in the surface tension - $\ln c$ plots changes, suggesting that at this concentration association state abruptly changes, such as the formation of micelles. The discontinuities observed in this study are not so distinct as the case reported for pyridine solution of a petroleum asphaltene by Sheu et al.(22) The discontinuity concentration for the petroleum asphaltene was also found to be about 0.03 g/dL, one order lower than those for the coal extracts, reflecting the difference of micelle structures probably due the difference between chemical structure, molecular weight and shape of both constituents. For PS from the same coal as AS, on the other hand, discontinuity was not observed. Further study is needed to clarify this.

Small-Angle Neutron Scattering

Although small-angle neutron scattering (SANS) studies on the size distribution and shape of petroleum asphaltene associates in solution have been actively carried out, only a few SANS studies on coal-derived substances were reported so far. Cody, Thiagarajan et al.(23,24) measured SANS of deuteropyridine solutions of pyridine extracts and their O-methylated derivatives. Laser desorption mass spectrometry of the extracts, untreated and methylated, indicates a predominance of relatively low mass materials, with molecular weight of the order 300 and a mass envelope which tails off around a thousand daltons.(23) SANS indicates that the solution structure of the extracts exists as small particles, with radii about 80 Å, and the values of fractal dimension, d (<3) indicates that the small particles further form a randomly assembled, loosely extended aggregates. Considering the molecular weights and radii for the particles, the elemental particles are themselves aggregates of the extract molecules. O-methylation is expected to decrease aggregation and/or make aggregates more loose, since hydrogen-bonding interactions are considered to constitute the dominant associative interparticle interaction. However, the change in the solution state due to O-methylation was found to be slight, and it induces more dense packing of aggregates for the two coals, in which d increases by O-methylation.

SANS data on the CS₂/ NMP mixed solvent extracts in solution by Cody, Thiagarajan et al.(25) are interesting. The solution of pyridine insoluble / the mixed solvent soluble component, PI in the mixed solvent contains no large aggregates, but the solution of pyridine extract from the same coal, which may be a lighter component than PI, contains large aggregates, though a light component seems less aggregative due to low content of functional groups. Recently we found that addition of 2 wt% of TCNE relative to the amount of PI results in an enormous change in the SANS behavior, namely, the addition of TCNE reduces the particle (associates) size greatly. This agrees with the enhanced extractability and solubility in CS₂/ NMP mentioned above by the addition of TCNE, considering that the size reduction of the associates of coal molecules makes

themselves more soluble in CS_2 /NMP. This result seems to give a direct evidence for the dissociation of the aggregates of coal molecules by TCNE through its strong interaction ability with coal molecules. However, our recent results (10) shows that some derivatives formed from TCNE may be responsible for the increase in solubility, rather than TCNE itself. So, the mechanism seems more complex than we considered so far. Further detailed study on the effect of TCNE and other additives such as PCP on SANS behaviors of coal extract solutions is needed to clarify the mechanism for the enhanced extractability and solubility in CS_2 /NMP.

Sol-Gel Transition

To date, no experimental data on sol-gel transition lines are reported on coal related materials. We are trying to address this important gap by direct measurement of sol-gel transition lines of coal related material-solvent mixtures. Our attention is focused upon thermoreversible gelation of coal extracts in organic solvents.

Many earlier studies have approached this problem by investigating rubbery or gelly coal - solvent and extracted coal - solvent systems (26-28). Based on studies of polymeric gels, it was generally believed that mostly relatively "poor" solvents were capable of gel formation. However, physical-thermoreversible gelation can take place in good solvents due to compound-compound and compound-solvent interactions. This kind of molecular aggregation has been widely observed in polymer-solvent systems, where gels are formed on cooling and disappear on heating. In contrast to the high molecular weight polymers, it has been discovered lately (29) that some lower molecular weight organic compounds (300 - 1000 daltons) can form thermoreversible gels with some organic solvents. Likewise, we have also observed that 2-naphthol (MW = 144 daltons) can form gels with N-methyl-2-pyrrolidinone (NMP). Intuitively speaking, the thermoreversible gelation could be a common feature in organic compound - solvent systems.

In this work we are interested particularly in the thermoreversible gelation in good solvents. Here, we introduce our preliminary approach to make direct measurements to determine the sol-gel transition lines for coal extracts and extract fractions using methods developed for polymer-solvent solutions. So far, no detailed thermodynamic analyses are attempted. In the present program of study we have been using various methods: a standard differential scanning calorimetry, a ball drop method and a thermogravimetric technique. A ball drop method was used to study "gel melting" lines. Experiments were carried out by cooling samples slowly to -30°C and then observing capabilities of solutions to keep 60 mg balls during heating with a rate about 0.5 °C/min. This type of experiment allows us to classify a substance presumably as a "gel" if its network is sufficiently stiff to withstand the 60 mg ball drop due to gravity. Preliminary experimental results using various extracts from Upper Freeport coal will be shown.

Computer Simulation

Computer-aided molecular design (CAMD) has been utilized in the designs of the drugs and new functional materials. Recently, it has been applied to coal.(30-33) Energetically stable three dimensional structure (conformation) of the extract fractions of coal was constructed by computer simulation.(33) The most stable structure in the energy-minimum state for model molecules PS, obtained from the CS_2 /NMP mixed solvent extraction of a bituminous coal was estimated to be an associated structure and the π - π interactions between aromatic ring systems play a major role to form the association.

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